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of

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and

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Table of Contents

I. Introduction

Research in the area of Materials Science and Solid State Physics and Chemistry at Rice University has been supported principally during the past eight years by National Aeronautics and Space Administration Grant NsG-6-59. The goals of this grant have been the following:

1.) To promote the growth of significant research in solid materials.

2.) To broaden the competence of workers in the area of solid materials.

3.) To encourage interdisciplinary cooperation in the field of solids at all levels.

To achieve these goals, funds from this grant have been used to support research in areas involving workers from six departments. As a consequence of this support, during the past six months we have accomplished the following:

1.) The program involved 17 faculty members, 33 graduate students, and 11 post doctoral fellows. Significant research results bearing on basic problems in solid materials have been obtained. These results are described in Section II.

2.) A new seminar program for faculty and graduate students interested in solid materials has been initiated.

3.) Interdisciplinary contact and cooperation have increased greatly since the occupancy of part of the new Space Science building by workers in materials science from many departments.

The Research Report given in Section II has a different format than that of previous progress reports. We have attempted to divide the research work on solids into five major areas; a status report for each area has been prepared by a staff member in that area. These reports are less technical and more descriptive than has formerly been the case. An attempt has been made to place the work at Rice in

perspective with respect to the whole field of solids as well as provide a report of recent progress. This initial attempt leaves much to be desired, but we hope to improve these reports so that they may be of wider use to those who receive them.

This year, a successful interdisciplinary seminar has been organized. It is a working seminar in which both faculty and graduate students present reviews and describe current progress in their research areas. Recent topics were:

1.) Tunneling in Superconductors

2.) The Theory of Dislocations

3.) Magnetism in Thin Films

4.) Observation of Defects by Electron Microscopy

5.) Thermodynamic Properties of Solid Solutions

6.) The Gravitationally Induced Electric Field in a Metal.

These seminars have proved very stimulating; there is a healthy interchange of ideas between people with quite different perspectives in solid materials.

A list of publications accepted during the period of this report is given in Appendix I. A financial report for this period is given in Appendix II.

II. Research Report

The research work on solids of 31 different projects supported by this grant divides naturally into five areas:

1.) Defect Structure and Mechanical Properties

2.) Electrical and Optical Properties

3.) Magnetism and Superconductivity

4.) Thermodynamics and Solid Surfaces

5.) Thin Film Properties

A report has been prepared in each of these fields by one of the research staff in that field. These reports are given below, together with a listing of the staff working in each field. The reports are intended to present some perspective on the field in question, as well as enumerate recent research accomplishments. Further details of some of this work may be found in the publications listed in Appendix I.

A. Defect Structure and Mechanical Properties--J. M. Roberts

Staff: F. R. Brotzen, Professor of Materials Science
J. M. Roberts, Associate Professor of Materials Science
M. L. Rudee, Assistant Professor of Materials Science

Four types of primary defects which occur in solids are chemical impurity atoms, vacancies, interstitials and dislocations. Studies at Rice University under the above heading are directed towards a better understanding of the properties of each of these types of defects as single entities in certain specific systems as well as their binary and multiple interaction with themselves and with one another.

The workers at Rice University have isolated three types of defect interaction problems which remain unsolved to date. This group feels these are fundamental problems to be solved so that a better understanding of the mechanical behavior of certain solid state systems can be acquired. Other studies are also being conducted which are related to these three major problem areas although not in a direct way. A brief description of the title and scope of each of these three basic problems will now be given.

(1) Plastic Deformation of Body-Centered Cubic Crystals

A fundamental understanding of the mechanical behavior of body-centered cubic metals has intrigued physical metal-

lurgists not only because of the scientific aspects involved, but also because of the far-reaching technical importance of the subject. In contrast to metallic crystals with a face-centered cubic crystal structure, body-centered cubic metals undergo drastic hardening and cease to be ductile at low temperature. The advent of lattice-imperfection theory has provided a means of gaining an understanding of the basic processes that take place in these materials during deformation. Nevertheless, no definite mechanism has been found to date that can explain fully the strong temperature dependence of the properties of body-centered cubic metals and alloys. It is the scope of a comprehensive program at Rice to investigate the deformation of body-centered cubic metals in order to try to isolate a definite mechanism or group of mechanisms which dictates this type of mechanical behavior in body-centered cubic metals.

(2) Experimental Verification of the Relation Between Short-Range Order (SRO) in Alloys and Their Electrical Resistivity

In binary alloys of metals there are two idealized states or arrangement of the two kinds of atoms in the crystal lattice: completely random or completely ordered. In reality, these limiting states are rarely attained, and most real solid solutions are in an intermediate state of local order. In this condition, there are again two alternative deviations from randomness. In one, atoms of like kind tend to be nearest neighbors; this is called clustering. The other deviation from randomness is called short-range-order and is produced when unlike atoms tend to be nearest neighbors. One is able from conduction theory and from x-ray diffraction theory to

predict how the degree and nature of short range order should affect the electrical resistivity and diffuse scattering in x-ray diffraction experiments. These relations are not simple, since the resistivity of the alloy may be expected to either increase or decrease, depending on the relative values of the SRO parameters. Careful measurements of the degree of SRO in a single crystal (by diffuse x-ray diffraction studies) as well as electrical resistivity studies of the same crystal over a range of temperature have not been previously made. It is the purpose of this research to carry out such a study to obtain definitive data relating the SRO parameters to electrical resistivity and hence to test the existing theories for this problem.

(3) Microstrain, Microcreep, and Amplitude Dependent Dislocation Damping in Metal Crystals

For about 20 years, physical metallurgists and solid state physicists have studied intensely the internal friction of metals and alloys as well as the flow stress or yield stress of these metallic systems. The internal friction has been studied in the frequency range of 10^{-1}cps to 10^{8}cps over wide temperature ranges. For most of these studies (via the damping of a torsion pendulum or acoustic attenuation of sound waves) the internal friction is stress or strain amplitude dependent and the anelastic strains are only a small fraction of the elastic strains. Their maximum value is about 10^{-2} of the elastic strain. At the yield point, however, the plastic and anelastic strain becomes very large, being several times

the elastic strain. The yield point seems to be a unique point on the stress-strain curve where gross departure from almost elastic behavior of the material occurs.

The entire region, wherein the anelastic and microplasticity properties of the solid increase from 10^{-2} of the elastic strain to approximately five times the elastic strain, has not been subject to a great deal of investigation. This is precisely the region where microcreep (plastic deformation of the solid in the strain rate range 10^{-9} to 10^{-2} sec^{-1} at constant stress) occurs, as well as the region where the internal friction or damping becomes strongly amplitude dependent. In this region we lack adequate experimental data upon which to formulate theories to predict the behavior of the solid, and conversely dislocation theory falls short of providing adequate microcreep, microstrain and amplitude dependent damping theories to even attempt to explain completely the limited data available.

Microstrain studies are interesting and important not only from the academic point of view as outlined above, but also because they have practical applications. Microstrain studies investigate in detail the nonelastic behavior of the solid undergoing strains in the region 10^{-7} to 10^{-2}. (The lower limit is not a true limit, but is simply determined by the limit of resolution of our existing strain sensing techniques.) Such small strains occurring in components of inertial guidance systems can cause malfunction. This work is a direct quantitative study of low cycle, low frequency,

moderately high amplitude fatigue, a rather common set of conditions in many metallurgical applications.

Current Status of Studies on Defect Structure and Mechanical Behavior

A brief review of the major findings of the recent studies at Rice on defect structure and mechanical behavior will be presented as well as an outline of the future plans for these studies.

(1) Plastic Deformation of Body-Centered Cubic Metals

A series of critical experiments have been carried out with molybdenum single crystals. This metal was chosen because it can be obtained readily in rather pure form, because single crystals can be produced with relative ease, and because the temperature dependence of its properties is pronounced. Since the slip system in body-centered cubic crystals is not clearly defined, most of the deformation experiments have been performed in direct shear on the most important slip system (110) $[1\bar{1}1]$.

This research with molybdenum crystals, under the direction of Professor Franz Brotzen, has been divided into the following phases:

(a) The careful determination of flow stress and activation volume as functions of temperature, strain rate, orientation, and strain in crystals of high purity.

(b) The study of the dislocation structure as a function of temperature, strain, and flow stress by means of direct observation (electronmicroscopy) and indirect observation (electrical resistivity).

(c) Research on the effects of small amounts of impurity on the mechanical properties of molybdenum crystals.

(d) A fundamental investigation of the effects of large amounts of soluble additions (rhenium) on the mechanical behavior of molybdenum crystals.

These studies revealed that, as a result of thermal activation, dislocation movement in molybdenum meets with increasing resistance at low temperatures. This apparent rise in the "frictional stress" is particularly pronounced in screw dislocations whose motion at low temperatures is greatly reduced. The high resistance to screw-dislocation motion is associated with very small activation volumes, and, significantly, with the generation of a uniform dislocation distribution of high density. The exact distribution and the density of the dislocations depends on the temperature of deformation and the strain rate. The dislocation structure changes drastically when the deformation is carried out near or above room temperature. The temperature dependence of this structure manifests itself also by a pronounced temperature sensitivity of the structural stress (τ_g)*. The structural stress tends to rise rapidly during the initial stages of deformation and can be varied by subsequent deformation at different temperatures.

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* The structural stress, τ_g, is defined as the difference between the applied stress, τ_a, and the internal stress, $\overline{\tau}$, which is the net stress acting on the dislocations at their points of activation. $\overline{\tau}$ represents principally the effect of the stress fields of all dislocations in the crystal on one given moving dislocation at a point of activation.

These observations were made not only through experiments in which the flow stress was measured at constant strain rate, but also through transient-creep experiments in which the applied stress was kept constant and the change in strain rate was observed while progressively changing the strain over small increments. Electrical-resistivity measurements (which yield dislocation densities after the appropriate subtraction of the resistivity component due to point defects) have borne out these trends and given a fair idea of the relation of dislocation densities to the structural stress.

Small amounts of interstitial impurities, such as oxygen, nitrogen, or carbon, are generally thought to produce sizable effects on the flow stress. The exact amounts of these impurities are difficult, if not impossible, to detect by analytical methods. The ratio of the electrical resistance at room temperature to that at liquid-helium temperature, however, is sensitive to the impurity content and has been used here with good results. A change in the resistance ratio, and therefore in the purity of the crystals, alters the stress-strain curve and the activation volume. The changes, however, were not as large as originally expected. This dependence on impurity content was very sensitive to the temperature of deformation. At low temperatures, the effect was limited to the early stages of deformation and was obliterated by work hardening. Increasing temperature tended to diminish the influence of impurities. At 350°K and higher, the effect of small amounts of impurities was below the limit of detection. At these temperatures, the stress-strain curve

begins to show features characteristic of the three-stage hardening obtained in face-centered cubic crystals. The higher the purity and the lower the strain rate, the greater was the similarity to the face-centered cubic behavior.

The addition of large amounts of rhenium soluble in molybdenum is known to improve the low-temperature ductility of the material. Investigations presently under way are aimed at using this phenomenon as a means for the determination of the mechanism of low-temperature hardening of body-centered cubic crystals. As a first step, the effect of the alloy additions on the elastic anisotropy of molybdenum will be established through a determination of the elastic constants of molybdenum as functions of rhenium content and temperature. If rhenium additions, as expected, affect the anisotropy of molybdenum, the observed behavior of the screw dislocations might be explained. Further work will then give a comprehensive picture of the mechanical behavior at low temperature in alloy crystals of varying rhenium content and will aim at a correlation with the elastic properties.

The general picture, which emerges from this series of investigations, although not complete, indicates that deformation at low temperatures proceeds with initially rapid multiplication of dislocations. A large number of dislocations is required to maintain the applied strain rate in view of the low dislocation velocity at these temperatures. This is accompanied by a drastic rise in the structural stress, τ_g. The multiplication of dislocations requires some motion of screw dislocations which can

occur only at suitably high stresses. The actual mechanism responsible for the low mobility of screw dislocations at low temperatures can only be guessed at this time.

(2) Experimental Verification of the Relation Between Short-Range Order (SRO) in Alloys and Their Electrical Resistivity

It is the purpose of this research, under the direction of Professor M. L. Rudee, to make careful measurements of the degree of SRO in a single crystal and also to measure the electrical resistivity of the sample from room temperature to 4.2°K. The state of SRO in a sample is characterized by a set of parameters that are related to the probability of finding unlike neighbors at the various neighbor distances, viz., first nearest neighbor, second nearest, and so forth. These parameters can be determined from the diffuse scattering in x-ray diffraction experiments. To obtain values of the SRO parameters for distances greater than second nearest neighbors, a single crystal sample must be used and great experimental care must be exercised. Various degrees of SRO will be produced by changing the thermal history.

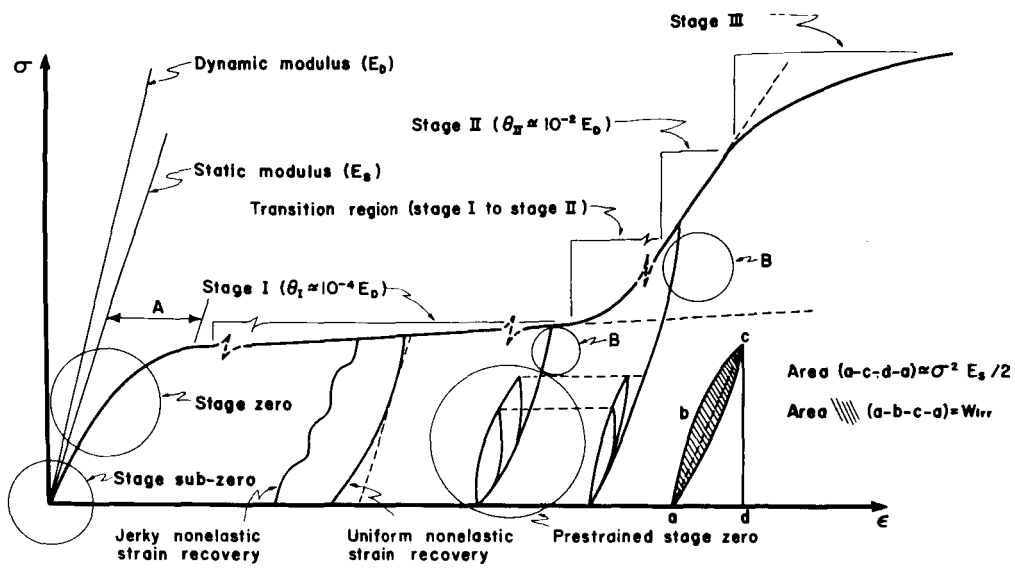
The necessary x-ray equipment has been assembled and carefully aligned. It had originally been planned to perform this experiment on the gold palladium system and a properly oriented single crystal had been obtained. This system seemed ideal for these experiments on the basis of some research performed by others. After great care had been exercised in producing an accurately oriented and smooth face for the x-ray measurements, it was observed that contrary to the reports in

the literature, no quenching treatment that we could devise produced anything other than a high degree of long-range order. Presently, the Ag-Mg and Cu_3 Au systems are being investigated along similar lines.

Concomitant with the experimental program, a seeming contradiction in the theory of x-ray diffraction from binary alloys has been resolved; this work was recently published in the Journal of Applied Physics.

(3) Microstrain, Microcreep and Amplitude Dependent Dislocation Damping in Metal Crystals

It seems that almost all metallic single crystals, under suitable conditions, exhibit three stages of work hardening, stages I, II, and III as shown in Figure 1.



Stage sub-zero $\{\Delta E/E_D \simeq 10^{-3}$ (max.) (modulus defect)$\}$ $\{2 W_{irr}/\sigma^2 E_D = \Delta \simeq 10^{-2}$(max.)= max decrement.$\}$
Stage zero and prestrained stage zero $\{\Delta E/E_D \simeq 10^{-1} = E_D - E_s/E_D\}$ $\{10^{-2} \leq 2W_{irr}/E_s \sigma^2 \leq 1$ decrement.$\}$
Stage zero for annealed crystals — the first loading of the crystal exhibits permanent plastic strain.
Prestage I or stage zero strain usually falls in the range $10^{-5} \leq$ to $\leq 10^{-3}$.
Region B is that of forward microcreep. Creep rates in the range 10^{-9} sec.$^{-1}$ to 10^{-6} sec.$^{-1}$ are usually noted.

SCHEMATIC ROAD-MAP OF MACROSCOPIC AND MICROSCOPIC UNIDIRECTIONAL STRESS-STRAIN CURVE

Figure 1

In this figure, the ordinate is the applied stress, σ, and the abscissa is the resultant strain $\mathcal{E}$. The red line indicates the general form of the observed macroscopic stress-strain curve. θ is simply the slope of the stress-strain curve at a particular value of $\mathcal{E}$ and is called the work-hardening coefficient. The detailed structure shown below the red macroscopic stress-strain curve is what can be observed using microstrain techniques upon unloading from a point (a fixed value of $\mathcal{E}$) on the red curve. If an extremely sensitive strain gauge is not used, the relaxation of stress (σ) at almost constant $\mathcal{E}$ can be studied, which also furnishes data regarding dislocation-dislocation and/or dislocation-primary defect interactions under quasi-static conditions. That is, detailed studies of the structure beneath the macroscopic stress-strain curve contributes quantitative data regarding dislocation interaction dynamics under conditions where no large scale motion of the defects occurs and where there is virtually no production of new defects.

A general study of the effects of impurities, stress amplitude, temperature and strain rate upon the details of microstrain (e. g., damping loop a-b-c-a) in Figure 1 and microcreep in zinc, magnesium, copper and molybdenum has been carried out under the supervision of Professor John Roberts. In all of these studies the plastic and anelastic strain rates cover the range 10^{-9} to 10^{-2} sec $^{-1}$, and the stress range usually studied is between 0 and G x 10^{-3}, where G is the shear modulus. The temperature is varied between 77°K and 400°K.

In the case of the work on magnesium single crystals, it seems clear that the loop of the type (a-b-c-a) in Figure 1

can be explained in terms of the interaction of two repulsive dislocations, the mobile (glide) dislocation cutting through the immobile (forest) dislocation by a thermally activated process. In some cases, pairs of dislocations do not repel one another, but attract to form a strong junction. Whether a pair of dislocations attracts or repels depends upon the relative orientation of the line axes and Burgers vectors of the two interacting dislocations. The studies on copper single crystals indicate that between 77°K and 300°K, it is the destruction or breaking down of attractive junctions that is the primary origin of the energy loss (i.e., mechanical work expended as heat as given by the area in the loop a-b-c-a).

Quantitative calculations have been made to determine the dependence of the energy loss of a loop (such as a-b-c-a in Figure 1) upon the stress, temperature, strain rate and structural parameters, for attractive and repulsive dislocation junctions.

The circled regions in Figure 1 labeled stage zero and stage sub-zero are more difficult to analyze, since the structure can change in each of these regions during testing. The precise way dislocations can multiply in these regions is not yet fully understood. Further quantitative studies are needed in this area since they reveal what happens to a metal the very first time it is slightly stressed. The details of exactly how the stress-strain curve (in red, Figure 1) approaches the modulii lines shown in Figure 1, (i.e., E_D or E_S) is a very important point, since this gives information regarding the friction stress resisting dislocation motion.

Various methods have been employed to study microstrain, but in this laboratory the capacitance method has been primarily used. A review article describing the use of capacitance gauge sensors to make precision mechanical property measurements has been prepared, presented, and will be published as part of the proceedings of the ASM Symposium held in Atlantic City, summer of 1966, concerning the general area of microstrain measurement.

Compatible with microstrain studies, are studies of microcreep. These studies involve following the time dependent low strain rate ($\simeq 10^{-9}$ to 10^{-5} sec^{-1}) of a specimen subjected to very small stresses. An investigation of microcreep in magnesium and molybdenum single crystals has been carried out in this laboratory. This work has been pursued using both techniques of measuring microcreep, i.e., stress relaxation at constant strain and strain relaxation at constant stress. The results have been very interesting since they yield independent checks of one set of data against the other. Dislocations following small displacement feel the stress fields of surrounding dislocations. Microcreep studies give a semi-direct measurement of the average value of this internal stress field ($\overline{\tau}$ previously described in II-a) resisting dislocation motion over a small strain increment. The stress relaxation studies on molybdenum indicate that a change in the mechanism of dislocation motion occurs at about 225°K. This is consistent with the different types of dislocation structure observed in molybdenum by thin film electron transmission studies previously described in this part.

(4) Ultrasonic Attenuation in LiF, Nb and Ta Crystals in the Megacycle Frequency Range From 2°K to 300°K

Professor Roberts is also interested in dislocation displacements of less than one interatomic distance. When vibrated at high frequencies and low amplitudes the dislocations interact with both the phonon and electron gas of the lattice, (the dislocation is displaced one or two atomic distances). The phonon interaction is fairly well understood and gives rise to an overdamped dislocation resonant peak in the megacycle frequency range. A knowledge of the temperature dependence of the damping constant due to phonons and electrons is fundamental to the understanding of exactly how these interactions occur. Further detailed studies are needed, and metals exhibiting superconductivity at low temperatures are of interest, particularly for an understanding of electron damping. The dislocation-electron interaction in the normal and superconducting states has not yet been completely studied either experimentally or theoretically. Equipment has been designed and built to carry out such a study, and further work is in progress.

(5) Stage I Deformation in Hexagonal Close-Packed Crystals

Work carried out by other authors and Professor Roberts on zinc crystals deformed in shear and in tension and by Professor Roberts and colleagues on cadmium in tension (both h.c.p. metals) indicates anomoulous behavior in the temperature dependence of the easy glide slope (θ_1) as well as the flow stress, σ_F (Figure 1), and the activation volume in Stage I.

In an attempt to determine the origin of these contradictory and unexplainable results, tests have been made on cadmium crystals in direct shear along the (0001) basal planes in the $[11\bar{2}0]$ direction. These experiments are now almost complete. Crystals deformed and tested in direct shear do not yield any of the anomoulous and unexpected results, but specimens deformed in tension do rather consistently. It is now a major problem to understand why specimens deformed in tension can produce an easy glide slope θ_1 (Figure 1), yet yield peculiar temperature dependent flow characteristics. It is essential that we completely understand all of the geometrical aspects with respect to the deformation of metals in Stage I since it precedes the important Stage II and Stage III hardening. Hexagonal close-packed crystals have been used since they exhibit a long and easily measurable Stage I hardening. It now seems important to study the dislocation structure in some h.c.p. crystals deformed in Stage I: some in tension, others in shear. This is a very difficult experiment since the dislocations in zinc and cadmium are highly mobile at room temperature under very low stresses. This means the crystals should be deformed and immediately neutron irradiated under stress prior to preparing thin films for electron microscopy observations. Detailed studies of the slip lines of hexagonal close-packed crystals deformed in shear and tension to the same strain are obviously required to help solve this problem.

B. Electrical and Optical Properties--T. A. Rabson

Staff: L. E. Davis, Assistant Professor of Electrical Engineering
G. C. Jain, Associate Professor of Electrical Engineering
T. A. Rabson, Associate Professor of Electrical Engineering
M. L. Rudee, Assistant Professor of Materials Science
G. T. Trammell, Professor of Physics

Of the many techniques which have been used to probe the structure and properties of solid materials some of the most fruitful have been based on the interaction of electromagnetic radiation with the atomic constituents of the materials. Some of the current research at Rice University involves the interaction of alternating electromagnetic fields with matter, the frequency of the fields varying from the microwave range, 10^5 Hz., up through the visible, to the region in which the radiation is known as X radiation or γ radiation, 10^{17} Hz. Obviously, the details of the interaction and even the nature of the radiation vary considerably with frequency and consequently each project involves radically different techniques.

(1) Microwave Interactions

Professor Davis has been interested in studying the properties of ferroelectric materials in the microwave range. Barium titanate is a typical example of such materials. It possesses a residual electric polarization even with no external electric field applied, providing it is below the Curie temperature. However, this effect is usually masked by static charges which accumulate on the surface of the material. The property that the ferroelectric materials possess which is potentially more useful is that their electric displacement versus applied

field curve possesses a certain amount of hysteresis analogous to that observed for ferromagnetic materials, and the shape of the curve is frequency dependent. As a result of the above facts, the electric susceptibility possesses both a real component and an imaginary (lossy) component, the magnitudes of which are frequency dependent. The polarization is not a linear function of the applied electric field. As a result of the non-linear relation between polarization and applied field the electric susceptibility is dependent on the applied field and hence the velocity of wave propagation is also so dependent. Consequently, one could hope to build microwave phase shifters the amount of whose phase shift could be controlled by an externally applied d-c electric field.

It has been found that the losses in barium titanate are so large at microwave frequencies that its use in a phase shifter is precluded. A study has been made of the effect of indium doping on the imaginary part of the electric susceptibility at microwave frequencies. It has been observed that the doping has little effect even though it raises the d-c resistivity of the material considerably. The conclusion is that the losses at microwave frequencies must not be ohmic, but are rather due to dielectric relaxation effects and hence cannot be overcome by doping.

(2) Light Interactions

It is in the visible frequency range that radiant energy is most efficiently absorbed by semiconductors through the process of electron-hole generation. The energy thus absorbed can be directly converted to electrical energy if it is absorbed

within or near a p-n junction. The electric field of the junction sweeps the carriers apart and thus produces an electrical current. Such devices are known as solar cells because they can directly convert radiant energy, such as that from the sun, to electrical energy.

Methods to improve the efficiency of solar cells are under study by a group under Professor G. C. Jain. The internal electric field in the semiconductor is a function of the doping profile of the diffused impurities which create the junction. The efficiency of the solar cell depends on how efficiently the electric field separates the hole-electron pairs. Calculations have been made of the optimum doping profile to give the most efficient solar cell under various conditions. In addition, experimental techniques for achieving such doping profiles through accurate control of the diffusion parameters are under study. A diffusion furnace for accurately maintaining a homogeneous temperature over a large volume has been purchased using funds from another grant. By carefully controlling the temperature of the semiconductor during the diffusion cycle one should be able to attain the required doping profile.

Not only does a semiconductor junction serve as an energy conversion device, but it can also be used to measure radiant flux. Work is in progress at Rice to optimize the parameters for a photo diode. Although the techniques are similar to those mentioned above, the parameters to be optimized are different. One is more interested in achieving linearity of response rather than maximum efficiency.

In addition, there is a newly instituted project to study the direct conversion of heat to electrical energy through the thermoelectric effect in semiconductors.

Until six years ago man could not produce coherent electromagnetic radiation at frequencies above the microwave range. The successful operation of the laser in late 1960 gave man a source of such radiation. However, the radiation is not completely coherent. Associated with this fact is the fact that the polarization of the light output from certain types of lasers is a function of time and space. Dr. Rabson and some of his students have investigated the properties of a Nd^{3+} doped glass laser (optically pumped) and have found that the light polarization varies from one spike to the next, the duration of individual spikes being about 10 microseconds and the spacing between spikes being of about the same duration. Apparatus was built to measure the polarization with the necessary time resolution, and observations were made as a function of pumping energy. It was observed that near threshold each spike became essentially 100% polarized, although the polarization was different in each spike. Coherent radiation must necessarily be 100% polarized. The fact that the light becomes more polarized near threshold is therefore in agreement with the prediction that the light output should be more coherent at lower pumping energies. The polarization properties of light from Nd^{3+} ions in a calcium tungstate matrix have also been studied. This is of interest because the active ions are the same as in the Nd^{3+} glass laser, but the background matrix is different and possesses

crystal axes which the glass did not. In this second case, the polarization of the light again varies from spike to spike, but it tends to be related to the crystal axes.

It is planned to observe the effect of applying external magnetic fields to Nd^{3+} glass and calcium tungstate lasers to see if the polarization can be controlled externally through the Zeeman effect. A better understanding of the whole process by which electromagnetic radiation interacts with excited ions to produce laser action should result from these experiments.

In conjunction with the above studies a theoretical description of partially polarized light beams in terms of light described as a modified spin-one particle, using density operators, has been worked out.

Professor Rabson's group is also involved in a project in cooperation with Professor Margrave of the Chemistry Department. It involves development and application of a technique to use a ruby laser as a source to vaporize samples for analysis in a mass spectrometer. It is hoped that extremely small samples of surfaces from solids may be studied in this way. The first experiments will involve an investigation of silicon surfaces by this technique.

(3) γ Ray and X Ray Interactions

At the high frequency end of the spectrum are γ rays and X rays. Such radiation is not only incoherent, but because of the usual recoil of the emitting nucleus it has a rather large spectral width because of the Doppler effect. One of the more recently discovered phenomena associated with γ ray emission

is the Mossbauer effect according to which nearly monoenergetic γ rays are emitted from low lying, isomeric states of nuclei with essentially no recoil of the emitting nucleus. Because of the reciprocal nature of the γ ray emission process and the γ ray absorption process, almost recoilless absorption can also take place, and it also has a very narrow bandwidth. Because of the large scattering amplitude possessed by the nuclei at the resonant frequency, appreciable scattering will occur for γ-rays of this energy. A group under the direction of Professor Trammell has calculated the scattering dynamics for γ rays in solids including the effects of the orbital electrons as well as the nuclei. These calculations were made using the techniques of quantum electrodynamics whereas most of the previous work on related subjects was done using the so-called semiclassical technique whereby the field is treated classically but the nuclei and electrons are treated quantum mechanically. One interesting result is that multiple scattering effects are not significant in most instances.

One of the most promising applications of the effect described above is to X ray diffraction. Some of the most fundamental information regarding the microscopic structure of solids is obtained from x-ray diffraction patterns. The scattering from one elemental atom can be distinguished from that of another element by taking into account the difference in scattering amplitudes because of the difference in atomic structures. However, it is difficult to distinguish atoms of almost the same structure. If nuclear scattering effects are

quite different in the two atoms, as they must be if one is scattering X rays corresponding to a nuclear resonance of one of the nuclei, then one can easily distinguish the scattering due to the two types of atoms.

An experiment is being prepared to study the structure of various iron-nickel alloys using the above ideas. Iron and nickel have similar atomic structure. However, Fe^{57} has a low lying isomeric state. A source of radiation will be provided by a Co^{57} source which decays to Fe^{57} in the isomeric state which then decays to the ground state through the emission of γ radiation of the resonance frequency. This source will be placed at the usual site of the electron target in an X-ray diffraction apparatus. The sample which will diffract the γ rays will be an iron-nickel alloy which is enriched in the separated isotope Fe^{57} in order to show nuclear resonance effects.

C. Magnetism and Superconductivity--H. E. Rorschach, Jr.

Staff: H. C. Bourne, Jr., Professor of Electrical Engineering
P. L. Donoho, Associate Professor of Physics
W. V. Houston, Professor of Physics
H. E. Rorschach, Jr., Professor of Physics
G. T. Trammell, Professor of Physics

The magnetic properties of solids are determined by the motion of the electrons within them. The orbital motion is responsible for diamagnetic behavior, including superconductivity, and the orbital motion also affects the spin alignment, which is responsible for para- and ferro- magnetism. The character of the orbital motion is determined by

the forces that act on the electrons. These forces arise from an interaction of one electron with another electron or with the crystal lattice. Two basic types of behaviour can result. If the electron-electron interaction is strong enough, cooperative effects occur, leading to superconductivity or ferro magnetism. If the electron-electron interaction is weak, the behaviour of the electrons is determined by their interaction with the lattice and any external electric or magnetic fields. No cooperative effects occur, but the energy states of the free electrons can be modified in important ways. Theoretical and experimental work to investigate both cooperative and single-particle behaviour has been in progress at Rice during the last reporting period.

(1) Cooperative Effects

Atoms of the rare earth metals are characterized by a few rather tightly bound electrons (the 4f electrons) which give the atom its magnetic properties. In the bulk metal, these electrons interact through the intermediary of the free electrons responsible for the conduction of electricity. This interaction can be positive or negative, and of varying strength, depending on the relative lattice position of the 4f electrons in question. Either ferro magnetism or anti-ferro magnetism may occur, and many interesting magnetic structures can result. Professor Trammell and some of his students have made an exact calculation of the ordering pattern expected for Gadolinium. The magnetic structure has been found to be ferro magnetic at T=0°K, in contrast to previous approximate calculations which predicted an anti-ferromagnetic screw structure. However, the ordering pattern is extremely sensitive to the electronic structure

parameters (e.g. the Fermi momentum), and the pattern depends sensitively on their values.

At temperatures above T=0°K, the magnetic structure is disturbed by the presence of "excitations" (spin waves in the case of a ferromagnetic material). These are excited electronic states which can interact with the lattice. Professor Donoho and his students have studied these excitations by microwave resonance methods. Strong resonances presumably associated with the interaction of the magnetic and the elastic waves have been observed in a single crystal of Dysprosium. These resonances are a type of ferromagnetic resonance, and attempts are being made to correlate the resonance frequency and line width to other crystal properties, such as the magnetic anisotropy and magnetostriction. This phenomenon may prove to be an efficient method for the generation of high frequency phonons.

Other work on ferromagnetic ordering in thin films is being carried out by Professor Bourne. It is described in Part E.

Superconductors have become technologically important in recent years because of their use in high field magnets and in sensitive control and detection circuits. All of these uses depend on an understanding of the interaction of the superconducting electrons with a magnetic field. Some superconductors ("Type I") display a perfect diamagnetism. Any external magnetic field is shielded from the interior of the superconductor by currents induced in a very thin layer on its surface. Another class of superconductors ("Type II"), discovered in recent years,

permits the penetration of a magnetic field in the form of small circular current loops ("vortices") in a background of a superconducting matrix. An understanding of the properties of these vortices is important for all of the above applications and must be sought in terms of the basic electronic structure of the superconductor. Their formation and motion under the influence of external fields, their interaction with defects, surfaces, and with one another are all subjects of fundamental importance. The properties of vortices are being studied by several methods.

1. The penetration of vortices into thick films and thin plates of type I and II materials is under study by Professor Houston and some of his students. The specimens are prepared in the form of disks and mounted on a torsion fiber. A localized magnetic field is applied near the edge of the disk with a toroidal coil. The magnetic field penetrates through the superconducting plate in the form of a vortex structure, and the force necessary to drag this structure through the disk can be measured. Attempts are being made to interpret the results in terms of the basic properties of the vortices.

2. The motion of vortices when subjected to alternating fields has been investigated by Dr. Houston and some of his students through an extensive study of ac losses in superconducting wires of type II material. Magnetization measurements have been made both in the absence and presence of alternating currents to study the

pinning of vortices and the patterns of current flow. The influence of external magnetic fields has been studied. The ac losses can be reduced greatly by the application of a longitudinal magnetic field, and this phenomenon has been investigated as a function of field, current, frequency, and wire size. The results have been interpreted with some success within the framework of the vortex-pinning model of Anderson and Kim, but the effect of a longitudinal field cannot be easily fitted into this model.

3. The superconductive properties of molybdenum have been extensively investigated by Dr. Rorschach and his students as part of a program on the properties of molybdenum in cooperation with workers in Materials Science (see Part A). The critical field has been determined as a function of temperature, and magnetization curves obtained for a number of samples. Magnetic hysteresis has been observed in quite pure samples: a complete expulsion of the field does not occur when the superconducting state is formed in the presence of a magnetic field. This is quite unexpected for a type I superconductor and can only be explained by the formation of a metastable state in which the flux is trapped by the surface currents in a vortex-like structure. This trapped flux disappears smoothly and reproducably as the magnetic field is reduced. Attempts are being made to interpret this

phenomenon in terms of the known properties of vortices interacting with one another and with the surface currents.

(2) Independent Particle Effects

If cooperative effects do not occur, then the electrons will have energy states determined by their interaction with the crystal lattice and with external electric and magnetic fields. The nature of this interaction can vary between wide limits, and it plays an important role in determining the magnetic properties of the solid.

In the perfect crystal, the electrons move under the influence of the lattice and any external magnetic field. This is an important problem which cannot be solved exactly; it requires the development of simple models which still retain the important characteristics of a real metal. Dr. Chambers, a postdoctoral fellow in physics, has developed a relatively simple two dimensional model to describe the motion of the electrons. The complex real metal has been replaced by a simpler model ("effective Hamiltonian") which still retains the features important for comparison with experiment. The phenomenon of "magnetic breakdown" (the electron tunnels from one energy band to another) has been taken into account and the magnetic oscillations associated with changes of field (de Haas-van Alphen effect) described. This model should provide a convenient model for the interpretation of experimental studies of electronic structure.

The magnetic properties of insulating crystals are determined by electronic impurities, tightly bound to a localized

position by the electric fields in the crystal lattice. These electric fields modify the energy states of the localized electrons and influence the resonant absorption of energy by the electron. Dr. Donoho and some of his students are studying the influence of an external electric field on the resonant absorption by the use of electron spin resonance techniques. The resonance is affected by the interaction of the electron with the lattice, and this can be modified by the application of an electric field. The location and charge state of meighboring ions can be investigated, and these workers hope to be able to clarify the nature of the interaction of the electrons with these ions. Neodymium ions in Calcium Fluoride are presently under investigation in an effort to understand some anamolous electron relaxation effects in this material.

D. Thermodynamics and Solid Surfaces--R. B. McLellan

Staff: R. Kobayashi, Professor of Chemical Engineering
J. L. Margrave, Professor of Chemistry
R. B. McLellan, Assistant Professor of Mechanical Engineering
Z. W. Salsburg, Professor of Chemistry
R. L. Sass, Professor of Chemistry

Various investigators working under the NASA Solids Grant at Rice are involved in loosely coordinated studies aimed at achieving a closer understanding of the nature of a wide variety of solids. The research is broadly based on experimental thermodynamic and kinetic studies, but at the same time theoretical calculations are being made on models involving bulk solids, solid surfaces, and diffusion mechanisms in solids.

Much of the experimental work involves the equilibrium conditions between the solid and a gas. Since the thermodynamic parameters in the

gas are either well-known or can be estimated, measurements of the variation of the gas-solid equilibrium with temperature give information on the thermodynamic functions of the solid. Such experiments have been carried out to obtain information on both bulk solids and solid surfaces. Thus the research described in this report will be categorized according to whether it deals with the bulk or surface properties of solids.

(1) Experimental Research on Bulk Solids

The specification of materials for high temperature applications requires an evaluation of the sublimation and vaporization process over the proposed temperature range. Modern techniques for such an evaluation include Knudsen and/or Langmuir weight-loss studies of sublimation or vaporization rates over a range of temperatures, coupled with a mass spectrometric examination of the vapors. These data allow one to establish the species present and the pertinent thermodynamic parameters, i.e., the heats, entropies and free energies. With the NASA-purchased Bendix time-of-flight mass spectrometer and the high temperature magnetic machine, the High Temperature Research Group at Rice under the direction of Professor J. L. Margrave, is carrying out vapor pressure measurements on elements (rare earths, refractory transition metals, silicon), on transition metal fluorides, and binary and ternary oxides containing silicon.

Work in the area of gas-solid interactions has also been performed on the thermodynamics of very dilute solid solutions; research is being undertaken at Rice by Professor R. B. McLellan which deals with solutions so dilute that solute-solute

interactions can be ignored so that the partial thermodynamic functions of a solute atom are the same as those of an isolated atom and furthermore the mixing statistics are very simple, enabling the configurational entropy to be calculated and thus separated from the total entropy. This allows the excess entropy (due to vibrational changes) to be extracted from experimental data. In previous work the vapor pressure of very dilute (<0.1 At.% solute) copper solid solutions containing silver and gold was measured over a wide range of temperature using a Knudsen effusion method. From the known thermodynamic parameters of the Cu and solute atoms in the vapor, their energy and entropy in the solid were extracted from the solid-vapor equilibrium data. Very large vibrational partial entropies were found ($\bar{S}_v \sim 7k$) and these results were explained using an elastic model to calculate the frequency perturbation of the matrix crystal when a solute atom is inserted. Effusion measurements are now being made on gold-based solutions containing solutes with a smaller radius than gold so that accurate vibrational entropy data can be obtained for solutions where the solute atoms act as negative centers of pressure.

Very dilute solutions containing interstitial solutes are also being investigated. Again the thermodynamic parameters of the solute atoms are obtained from vapor-solid equilibrium measurements, but in this case the equilibrium between the solutions and gaseous mixtures containing the solute atoms have been studied. The thermodynamic parameters of nitrogen and carbon in iron have been investigated by this means. Statistical mechanical models of more concentrated intersitital solid solutions

have been developed and it has been shown that the thermodynamic behavior of C in F.C.C. iron can be explained by a model in which a C-atom can prohibit an integral number of surrounding sites from being occupied. Future work will involve theoretical studies of dilute Fe-C-X ternary solutions, where X is a substitutional solute, and measurements of the C-activity in such solutions from the equilibrium between the alloy and $CO-CO_2$ mixtures.

Work has also been done on the diffusion of interstitial solute atoms. The curvature of an Arrhenius plot of D the diffusivity of C in B.C.C. iron at high temperatures (shown in Figure 2) has been explained by a model in which C can occupy both the octahedral and the tetrahedral intersititial sites. Only one C in 10^3 is located on a tetrahedral site so the dual occupancy is not seen in the thermodynamics of the

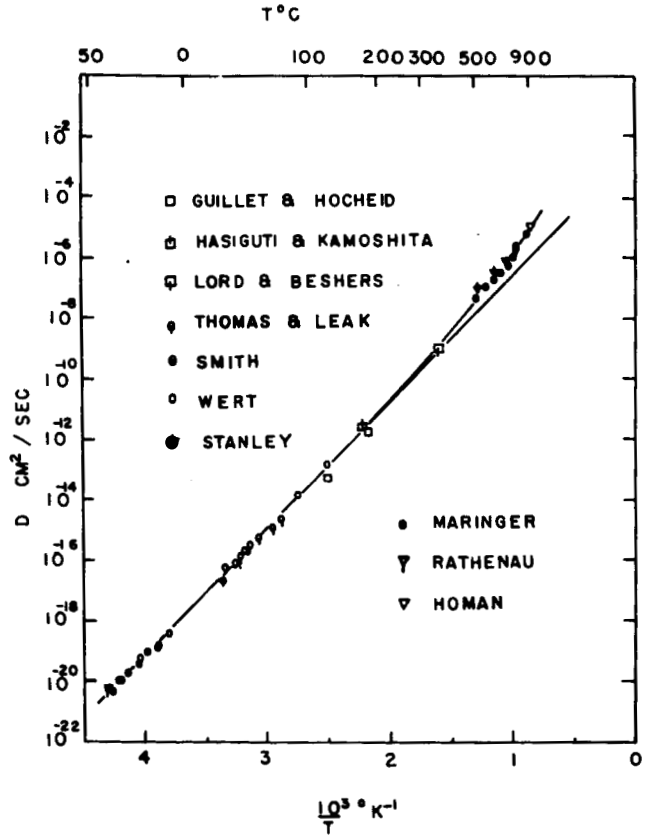


Figure 2--Plot of all the available data for the diffusion of carbon in α iron.

C-atoms, but since diffusion along tetrahedral sites is very much faster it makes a large effect on the total C-diffusivity.

At present, work is being undertaken to measure the diffusivity of C in δ-iron (the B.C.C. high temperature modification) by a penetration method. This should provide a good check on the theoretical model since the departure from linearity of the Arrhenius plot should be very large at high temperatures.

Professor R. Kobayashi and his group are making a study of the thermodymanics of gas hydrates. In this study it has been found possible to start from the various intermolecular potential functions and the crystal structure of the gas hydrates to calculate their decomposition pressures as a function of temperature. An extensive experimental program has also been carried out to study the circumstances under which pure and mixed gases form hydrates over wide pressure and temperature ranges. It is interesting to note that there is a strong possibility that gas hydrates may be the form in which water occurs in and about some of the outer planets.

Finally in the area of the experimental study of bulk solids Professor R. L. Sass and his associates are making X-Ray diffraction studies of the structure of complex molecules. These studies can be regarded as fitting in the area of the thermodynamics of solids since statistical mechanical calculations of the thermodynamic and transport properties of solids involve a knowledge of the positions of the atoms in the lattice. Certain molecules consisting of chains and/or rings of

alternating single and double bonds between carbon, nitrogen and oxygen atoms can exhibit bonding explainable in terms of delocalized electrons similar in nature to those found in metals. The observed effect of delocalization is a tendency for those molecules to assume a planar configuration. Graphite is an example of such a system. It is possible for forces between neighboring molecules in the crystal to distort these systems. The amount of distortion is a measure of both the crystal forces and the bending force constants within the molecules. Usually, the internal forces maintaining planarity are so strong that deviations due to the crystal field are too small to measure. Presently several new stable carbanions (complex ionic organic compounds) have been synthesized. These compounds should be rather easily distorted from planarity around the charged carbon atom. The crystal structures of five such compounds have been determined by the use of single crystal X-ray diffraction techniques. All show significant deviation from planarity. During the last six month period the structure of dipotassium tetranitroethanide was solved. The various N-O distances are all 1.25±0.02 Å; C-N = 1.38± 0.01 Å. The central C-C distance was found to be 1.47 Å. The ion is quite non-planar. The nitro-groups are rotated because of stearic effects and the trigonal carbon atoms are slightly pyramidal. Future plans resolve into a continuing study of these distortions as a function of crystal packing and differing molecular composition. A study of the infra-red spectrum of such compounds could then

determine the internal molecular force constants and thus give some indication of the crystal field forces in these complex systems.

Another line of research now under way is the determination of the bond distances and angles in small ring sulfones. The object of this work is to correlate the ring distortion, compared to similar sulfide rings, as a function of the C-S-C angle. Observations on the three membered ring of cis-2-butene episulfone show that for a highly strained C-S-C angle of 55.3°, the C-C single bond distance is 0.13 Å longer than that found in the corresponding sulfide system. The structure of the five membered ring in dibenzothiophene-5, 5-dioxide, in which the C-S-C bond angle is 91.6°, was found to be nearly identical to the corresponding sulfide system.

(2) Theoretical Research on Bulk Solids

An obviously important area in understanding the nature of solids is the investigation of the forces acting between atoms in crystals. In this context Professor Z. W. Salsburg is making a study of the anharmonic forces operating in theoretical models simulating loosely bound crystals. The dynamical effects in crystals are usually treated by expanding the potential energy in powers of the displacements from the static equilibrium positions. The harmonic approximation is obtained by

$$\Phi = \Phi_0 + \Phi_2 + \Phi_3 + \Phi_4 + \ldots,$$

Φ = potential energy function,

Φ_j = terms of j^{th} order in the displacement variables.

neglecting higher than second order terms in this expansion.

Anharmonicity is usually treated by making the normal mode frequencies of the harmonic approximation volume dependent (the quasi-harmonic models) or treating Φ_3 and Φ_4 by perturbation theory. Anharmonic effects are usually more important for more loosely bound crystals. This probably occurs because configurations corresponding to large displacements from the static lattice positions play an important role. Anharmonic effects are thus smallest for the ionic crystals and largest for van der Waals crystals. Anharmonic effects not only become important at high temperatures but also increase at higher pressures. Under high temperature and pressure conditions repulsive forces between the atoms dominate the attractive forces and the anharmonic terms become very large.

In order to obtain a better theoretical understanding of the role of anharmonic terms Salsburg has studied the most extreme anharmonic model--a solid of rigid spheres. This model approximates the repulsive forces between pairs of atoms as illustrated in Figure 3. The steeply rising repulsive potential is replaced by a vertical line. This model possesses no

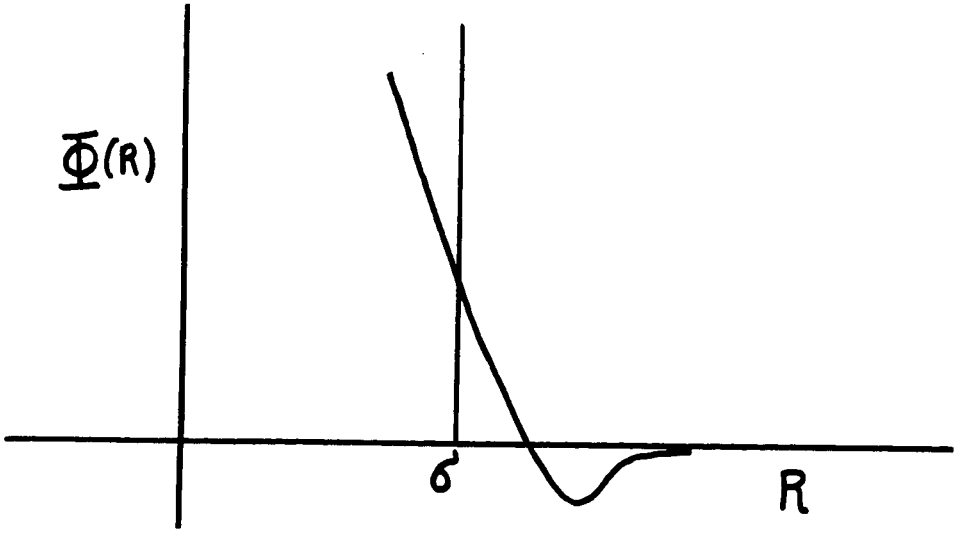


Figure 3

harmonic expansion. By looking at the difference between the harmonic model and the rigid core model one should be able to obtain some estimate of the maximum effect of anharmonicity in the potential. First of all, techniques for treating a hard sphere solid under compression had to be developed. This was done by a sequential method of approximation of evaluating contributions from the correlated motion of two particles, three particles, etc. An asymptotic expansion for the thermodynamic properties in the limit of close packing was also developed, and current work has only considered the leading asymptotic contributions to both the thermodynamic and elastic properties of hard sphere crystals. During the last six months the following calculations have been emphasized.

(a) Determination of the radial distribution function at high density - A sequence of approximations to the radial distribution function for a face centered lattice of rigid spheres is currently being developed using the approximation mentioned above. Analysis shows that the radial distribution function at contact between two spheres has a positive slope and negative curvature. This surprising result means that in a high density system of rigid spheres, two spheres almost in contact will be forced apart by the average force exerted on them due to the motion of the neighboring particles.

(b) Evaluation of elastic constants in rigid disk and hard-sphere crystals - The approximation technique mentioned above for evaluating the thermodynamic functions of rigid

molecules under high compression has been generalized to include distorted or strained systems. The resulting strain component variation of free energy then permits extraction of elastic constants, both linear and non-linear. So far, this analysis has been carried through for the two dimensional rigid disk model and for hard spheres in three dimensions in the face centered cubic lattice. For the latter case, the longitudinal to transverse sound velocity ratio for propagation along the 100 direction was evaluated. For hard sphere crystals in the hexagonal close packed arrangement, the results suggest that the crystal will exhibit a spontaneous small contraction along the c axis.

(3) Solid Surfaces

Many projects are being undertaken in order to obtain a more complete understanding of the nature of the surfaces of solids. Again much of this work involves studies of the interaction of a gaseous phase with the solid surface.

The research effort under the direction of Dr. T. W. Leland, Jr. in this phase of the Materials Grant is oriented toward a long term study of the role of surfaces in adsorption and in catalysis.

Some of the work completed, currently underway, and proposed for the future is as follows:

(a) A study has just been completed on the applicability of a mobile fluid model to describe physical adsorption on heterogeneous surfaces. This model has led to an improved

two-dimensional equation of state based on a van der Waals model with an ordering parameter contributed by the surface. This permits the prediction of physical adsorption equilibria for pure and mixed adsorbates over a wide range of conditions. Studies are planned for a similar approach to certain types of chemisorption.

(b) Studies are now underway to compare the electrical conductivity, Seebeck EMF, and capacitance change for compressed powders and single crystals of zinc oxide when exposed to chemisorbing CO and O_2 and reacting CO and O_2 mixtures. An extensive study has been completed on the apparent conduction electron concentration in polycrystalline cadmium sulfide obtained by using single crystal theories with Seebeck EMF measurements. This concentration was compared to the known electron concentrations brought about by the introduction of Cl^- impurities from the decay of S^{35} in the cadmium sulfide. The results showed definitely that the single crystal theories can have some applicability to polycrystalline materials. Conditions under which the calculations succeed or fail have been partially identified.

(c) Studies of the response of the Seebeck EMF and conductivity on polycrystalline films and powders are being used to indicate the extent of electronic equilibrium between bulk and surface regions. Since the Seebeck EMF measurement depends on the bulk properties to a significant extent there is apparently an inhibition of electronic

equilibrium between the bulk and surface. With zinc oxide powders a very pronounced effect on the Seebeck EMF accompaning the chemisorption and rate of change measurements indicates the time required to establish a definite electronic equilibrium between surface and bulk.

(d) Models for polycrystalline materials are being tested which assume a two-region crystallite. A bulk region is described by single crystal properties and a surface region is characterized by an electrical potential barrier between the crystallite. Models of this type have been effective in explaining chemisorption phenomena.

(e) A catalytic reactor has been built to measure reaction rates on single crystals and compare with rates on polycrystalline powders. Results are also being compared with the electrical measurements of Seebeck EMF and conductivity for the two catalyst forms.

Another apparatus is used to study the response of catalytic surfaces to ultravoilet light with carefully controlled frequencies from a monochromator. Data have been obtained which show the frequencies at which the reaction enhancement is greatest. These are being compared with known electronic transitions obtained from the ultraviolet absorption spectrum measured by other invesigators.

Research is also being carried out at Rice on surface ionization. Professor J. L. Margrave and his associates are studying this phenomenon, again using gas-solid interaction, and making measurements of the kinetics of gas-surface interactions.

In this project a study of the interaction of species of low ionization potentials (mono- and difluorides of various metals) is in progress. For example, when a beam of MF_2 molecules is directed onto a hot filament or ribbon of Ta, W, Pt, Ir, etc., MF^+ ions can be detected. From the temperature dependence of surface ionization processes the work function of the surface can be determined, and with time-resolved mass spectrometry the residence times and other kinetic properties can be measured.

Finally in the area of solid surfaces, Professor R. Kobayashi is making a study concerned with the application and extension of the principles of eblution gas chromatography to the adsorption of pure components and mixtures on a commercial adsorbent, i.e., silica gel. A recent development using a series of perturbing gases, e.g. He, Ne, Ar, etc., and extrapolation of the perturbation times energy-wise to obtain the perturbation times of a hypothetical gas of zero interaction energy has enabled the measurement of the volume occupied by the adsorbed species. The adsorbed volumes must necessarily be taken into account to accurately describe the adsorption isotherms in the high pressure region. Furthermore, it is now possible to present adsorption data rigorously in the form of classical Gibbs adsorption isotherms.

E. Thin Film Properties--M. L. Rudee

Staff: H. C. Bourne, Jr., Professor of Electrical Engineering

M. L. Rudee, Assistant Professor of Materials Science

When a ferromagnetic material is very thin, it is energetically favorable for the magnetization to lie in the plane of the film. Usually, such samples are produced by depositing the ferromagnetic material on to

an appropriate substrate from either a vapor or a chemical solution. In many materials, the application of an external magnetic field during deposition somehow alters the structure so that subsequently, in the absence of an applied field, the film's own magnetization prefers to be parallel to the direction of the field applied during deposition. The sense of the magnetization can then be switched by the application of an external field.

Devices of this sort, with two stable directions of magnetization, may be used as the basic memory elements in digital computers. Presently, most computers use a device with a toroid of a magnetic oxide as their primary memory element, but thin film elements can be switched from one direction to the other much faster and with less expenditure of energy than can conventional devices. Since minimizing these parameters is very important in computer design, thin film devices hold great promise for widespread application, and some special purpose computers are presently being constructed with them. It is also likely that a better understanding of magnetic films will lead to new magnetic devices.

Although it is possible to produce useful thin film devices, there are many fundamental questions about the nature and operation of these elements that are unanswered. For example, the origin of the grown-in uniaxial magnetic stability, the property that makes them useful, is still a topic of active controversy.

The research on magnetic thin films has been approached in two different ways. In one, the emphasis is on the dynamical properties of the switching processes. Experiments are conducted to measure the nature of the switching process and its hysteresis losses and to develop theoretical explanations of the results. For this research, equipment has been constructed to measure the hysteresis loss over a wide range of

switching drive rates and at various temperatures. In the lower ranges of drive rates, the rotation of the magnetization does not occur coherently across the sample. Instead the film switches by nucleation and growth of domains that possess the new direction of magnetization. These domains can be observed using polarized light (the Kerr magneto-optic effect), and equipment has been constructed to record dynamical observations of the domain pattern during switching using a pulse technique to achieve partial switching. Thus far most of the research in this area has been directed toward the determination of the dependence of the losses on switching rate in single-layer films at room temperature. Future work will emphasize the effect of temperature and the study of composite films formed by alternate layers of magnetic and non-magnetic material. These multi-layer films exhibit a much smaller coercive force and much less hysteresis loss.

In the second approach, various static magnetic properties are measured and related to structural properties, and these in turn are related to growth conditions. The emphasis of this research is directed towards gaining a physical understanding of some of the important properties of thin films, such as the origin of the anistropy.

For this research, equipment has been constructed to produce films under a wide range of conditions and to characterize their structural properties by a variety of techniques. These include electron microscopy and x-ray microstress measurements. In addition a torque magnetometer is under construction for very precise measurements of the magnetic properties. These techniques will be used on films produced under varying conditions and after differing annealing treatments.

APPENDIX I

Publications During The Period of This Report

A. Defect Structure and Mechanical Behavior

1. L. D. Whitmire & F. R. Brotzen,
"Easy Glide in Molybdenum Crystals"
Accepted for publication in Acta Metallurgica.

2. L. D. Whitmire and F. R. Brotzen
"The Effects of Deformation on the Electrical Resistivity of Molybdenum Single Crystals"
Accepted for publication in Trans. of the Metallurgical Society, AIME.

3. J. M. Roberts
"The Friction Stress Acting Upon Moving Dislocation as Derived from Current Microstrain Studies"
Accepted for publication in Acta Metallurgica.

4. J. M. Roberts
"A Note Concerning the Friction Stress Acting Upon Moving Dislocation as Derived from Current Microstrain Studies"
Accepted for publication in Acta Metallurgica.

5. T. Ishibachi & M. L. Rudee
"Singularities in the Coherent Diffuse Scattering of x-rays"
Published J. Appl. Phys. 37, 3559 (1966).

B. Electrical & Optical Properties

1. Sun Lu & T. A. Rabson
"A High Time Resolution Polarimeter for Laser Analysis"
Published Applied Optics 5, 1293-1296, August, 1966.

2. G. C. Jain & R. M. S. Al-Rifai
"The Effects of Drift-Fields & Field Gradients on the Quantum Efficiency of Photocells"
Accepted for publication in Journal of Applied Phys., Feb. 1967.

3. G. C. Jain & Sheng San Li
"Effects of Dimensions in Radiant Energy Conversion Cells"
Accepted for publication in IEEE Trans. of Aerospace & Electronic Systems.

C. Magnetism & Superconductivity

1. R. B. Hemphill, P. L. Donoho & E. D. McDonald
"Spin-Lattice Interaction in Ruby Measured by Electron Spin Resonance in Uniaxially Stressed Crystals"
Published Phys. Rev. 146, 329 (1966).

APPENDIX I

page 2

2. T. D. Black & P. L. Donoho
"Spin-Lattice Interaction for Ions with Unfilled f-Shells measured by ESR in Uniaxially Stressed Crystals"
Accepted for publication in Proc. Int. Conf. on Magnetic Resonance & Relaxation XIV Colloque AMPERE, North-Holland Publishing Co.

3. P. L. Donoho & T. D. Black
"Spin-Lattice Relaxation Time for Nd^{3+} and U^{3+} Ions in C_aF_2 in Sites of Tetragonal Symmetry"
Ibid.

4. W. G. Chambers
"Magnetic Breakdown: Effective Hamiltonian & de Haas-van Alphen Effect"
Published Phys. Rev. 149, 493 (1966).

D. Thermodynamics & Solid Surfaces

1. J. L. Margrave
"High Temperature Chemistry"
Published Encyclopedia of Chemistry, (Reinhold Publishing Co., New York), 1966.

2. K. F. Zmbov & J. L. Margrave
"Mass Spectrometric Studies at High Temperatures. XI. The Sublimation Pressure of NdF_3 and the Stabilities of Gaseous NdF_2 and NdF"
Accepted for publication, J. Chem. Phys., 1966.

3. J. L. Margrave, Editor
"Proceedings of Conference on Current and Future Problems in High Temperature Chemistry"
To be published, National Research Council, Washington, D. C.

4. J. L. Margrave, Editor
"Characterization of High Temperature Vapors"
In press, (J. Wiley & Sons, New York).

5. J. L. Margrave
"Physical Chemistry"
Science Year, World Book, 1966.

6. J. C. Thompson, J. B. Ezell, P. L. Timms and J. L. Margrave
"Chemical Reactions of High Temperature Species"
To be published in Advances in High Temperature Chemistry, Academic Press (1966).

APPENDIX I

page 3

7. J. D. McDonald, J. C. Thompson, C. H. Williams and J. L. Margrave "Silicon-Fluorine Chemistry. V. Appearance Potentials and Thermodynamic Properties for Si_2F_6, Si_3F_8, Si_4F_{10} and Si_2BF_7" To be published, Applications of Mass Spectrometry in Inorg. Chem. (1967), American Chemical Society.

8. Rex B. McLellan
"The Thermodynamics of Interstitial Solid Solutions"
To be published in "Phase Stability in Metals & Alloys"
McGraw-Hill, January, 1967.

9. Russell D. Larsen and Zevi W. Salsburg
"A Cell-cluster Development for the Pair Distribution Function: Application to Rigid Disks at High Density"
Journal of Chemical Physics.

10. Z. W. Salsburg, W. Rudd and Chemistry 420
"A Modified Cell-cluster Theory for the Solid State With Application to the Harmonic Model"
Physica.

11. Zevi W. Salsburg
"Rigid Disks and Spheres at High Densities: Bounds on the Partition Function"
The Journal of Chemical Physics, May 15, 1966.

12. Z. W. Salsburg and W. G. Rudd
"Tunnel Model for Rigid Disks Near Close Packing"
The Journal of Chemical Physics, August 1, 1966.

13. Zevi W. Salsburg
"Voids in a Crystal Structure of Identical Spheres"
Journal of Chemical Education, July, 1966.

14. Isamu Nagata & Riki Kobayashi
"Calculation of Dissociation Pressures of Gas Hydrates Using the Kihara Model"
I & EC Fundamentals 5, 344 (1966).

15. Isamu Nagata & Riki Kobayashi
"Prediction of Dissociation Pressures of Mixed Gas Hydrates from Data for Hydrates of Pure Gases with Water"
I & EC Fundamentals 5, 466 (1966).

E. Thin Film Properties

1. M. L. Rudee
"A Study of the Domain Structure of Carbon Black by Both High-Resolution Dark-Field Electron Microscopy and x-ray Diffraction"
Accepted for publication in Carbon.